

Supporting Information

Highly Fluorescent BODIPY Dyes Modulated with Spirofluorene Moieties

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Experimental Section

General. Unless otherwise specified, all reagents were purchased from a chemical supplier and used without further purification. Tetrahydrofuran (THF) was distilled over benzophenone ketyl under nitrogen atmosphere. *N,N*-Dimethylformamide (DMF) was distilled over MS4A under nitrogen atmosphere. CH₂Cl₂ was dried and collected using a Grubbs-type solvent purification system manufactured by Glass Contour. Melting points are uncorrected. ¹H and ¹³C spectra were recorded on a JEOL AL-300 (300 MHz for ¹H, and 75.5 MHz for ¹³C) instrument or a JEOL EX-400 (400 MHz for ¹H, and 100 MHz for ¹³C) instrument. IR spectra were obtained on a JASCO 460 plus FT/IR spectrometer. Mass spectra were measured with a JEOL JMS-SX102A. Analytical thin-layer chromatography (TLC) was performed on Merck 60F₂₅₄ silica plates and visualized by UV light. Column chromatography was carried out on Silicycle SilicaFlash F60 60-63 μm (230-400 mesh) silica gel. Preparative HPLC was carried out with a Japan Analytical Industry Co., Ltd, LC-908 chromatograph using a JAIGEL-1H and -2H GPC columns. UV-visible absorption spectra were recorded on a JASCO V-570 UV-vis-NIR spectrometer. Emission spectra were measured with a Jobin Yvon-Horiba FluoroMax-3. Degassed spectral grade solvents were used for the measurements. Absolute fluorescence quantum yields were determined by the calibrated integrating sphere system. Cyclic voltammetry (CV) was performed on a BAS ALS 610C-S electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and an

Ag/AgNO₃ reference electrode. The measurement was carried out under argon atmosphere using solutions of samples (1 mM) and 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as a supporting electrolyte with a scan rate of 100 mV s⁻¹. The redox potentials were calibrated with ferrocene as an internal standard.

9-(2-Bromophenyl)-9H-fluoren-9-ol (1)¹

The solution of 1-bromo-2-iodobenzene (34.9 g, 124 mmol) in dry THF (120 mL) was cooled to -40 °C. To the solution was added dropwise 1.0 M THF solution of isopropyl magnesium bromide (120 mL), prepared from isopropyl bromide and magnesium turnings. After stirring for 3 h, 9-fluorenone (14.4 g, 80.0 mmol) in dry THF (80 mL) was added over 25 min and stirred at room temperature for 12 h. The reaction mixture was quenched with saturated aqueous solution of NH₄Cl (100 mL) and extracted with EtOAc (3 × 30 mL). The organic layers were combined, washed with brine (2 × 50 mL), and dried over MgSO₄. The solvents were removed under reduced pressure to give a mixture of white solid and yellow oil. The crude product was purified by washing with hexane and the filtrate was purified with column chromatography on SiO₂ (EtOAc–hexane, 1:20) to give **1** (25.6 g, 95%) as a white solid; mp 145.2–146.0 °C. IR (KBr) 767, 920, 1005, 1157, 1333, 1448, 1604, 3063, 3571 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 2.39 (br s, 1H), 7.13–7.25 (m, 5H), 7.36–7.47 (m, 4H), 7.67 (d, *J* = 7.7 Hz, 2H), 8.44 (br s, 1H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 83.0, 120.2, 120.9, 123.9, 127.0, 128.3, 129.0, 129.1, 129.2, 134.3, 140.8, 141.3, 148.6.

9-(2-Bromophenyl)-9-(*N*-tosylpyrrol-3-yl)-9H-fluorene (2)

To a solution of **1** (9.72 g, 28.8 mmol) and *N*-tosylpyrrole (6.94 g, 31.3 mmol) in CH₂Cl₂ (200 mL) was added AlCl₃ (4.39 g, 32.9 mmol) portionwise, and the solution was stirred at room temperature for 3 h. The reaction mixture was quenched with water (60 mL) and extracted with CH₂Cl₂ (3 × 30 mL). The organic layers were combined, washed with saturated aqueous solution of NaHCO₃ (2 × 40 mL) and brine (40 mL), and dried over MgSO₄. The solvents were removed under

reduced pressure to give white solid. The crude product was purified by washing with CHCl_3 –hexane (1:1) and the filtrate was purified with column chromatography on SiO_2 (EtOAc–hexane, 1:20) to give **2** (14.5 g, 93%) as a white solid; mp 210.2–211.0 °C. IR (KBr) 605, 674, 746, 1065, 1101, 1172, 1253, 1371, 1464, 1596 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 2.36 (s, 3H), 6.40 (br s, 1H), 6.61 (br s, 1H), 7.01–7.09 (m, 2H), 7.14–7.40 (m, 11H), 7.59 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 7.7 Hz, 2H). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 21.6, 60.4, 115.6, 119.3, 120.4, 121.5, 123.0, 124.7, 126.76, 126.81, 127.4, 127.5, 128.6, 129.9, 131.8, 132.1, 135.4, 136.0, 141.1, 142.1, 144.9, 149.8. HRMS (FAB): calcd for $\text{C}_{30}\text{H}_{23}^{81}\text{BrNO}_2\text{S}$ ($\text{M}+\text{H}^+$), 542.0616, Found 542.0609.

1'-Tosylspiro[fluorene-9,4'(1'*H*)-indeno[1,2-*b*]pyrrole (3a) and 2'-Tosylspiro[fluorene-9,4'(2'*H*)-indeno[1,2-*c*]pyrrole (3b)

A flame dried flask was charged with **2** (14.5 g, 26.8 mmol), K_2CO_3 (7.57 g, 54.8 mmol), $\text{Pd}(\text{PPh}_3)_4$ (930 mg, 0.805 mmol), and dry DMF (200 mL) under nitrogen atmosphere. The solution was stirred at 100 °C for 20 h. The reaction mixture was cooled down to room temperature and filtered through a short silica gel pad. After an addition of water (150 mL), the filtrate was extracted with CH_2Cl_2 (3 \times 30 mL). The organic layers were combined, washed with brine (7 \times 50 mL), and dried over MgSO_4 . The solvents were removed under reduced pressure to give a mixture of white solid and brown oil. The crude product was purified by washing with CHCl_3 –hexane (1:1) to give **3a** (7.77 g, 63%) as a white solid. The residue was purified with GPC (CHCl_3) to afford **3b** (739 mg, 6%) as a white solid.

3a: A white solid; mp 256.5–257.3 °C. IR (KBr) 670, 699, 749, 1113, 1173, 1192, 1380, 1446, 1462, 1596, 3128 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 2.42 (s, 3H), 5.86 (d, J = 3.3 Hz, 1H), 6.52 (d, J = 7.3 Hz, 1H), 6.63 (d, J = 7.7 Hz, 2H), 6.93 (dd, J = 7.5, 7.7 Hz, 1H), 7.07 (dd, J = 7.3, 7.5 Hz, 2H), 7.22 (d, J = 3.3 Hz, 1H), 7.28–7.36 (m, 5H), 7.78 (d, J = 7.7 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 8.15 (d, J = 7.7 Hz, 1H). ^{13}C NMR (75.5 MHz, CDCl_3): δ 21.6, 60.2, 108.7, 119.5, 120.0, 123.5, 123.6, 125.7, 126.76, 126.81, 127.6, 127.7, 127.8, 130.0, 134.0, 135.9, 138.2, 139.9, 141.8, 145.1, 146.4, 152.5.

HRMS (FAB): calcd for $C_{30}H_{22}NO_2S$ ($M+H^+$), 460.1371, Found 460.1364.

3b: A white solid; mp 212.7–213.6 °C. IR (KBr) 673, 752, 1053, 1089, 1166, 1187, 1362, 1446, 1595, 3063 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 3H), 6.49 (d, $J = 7.3$ Hz, 1H), 6.67 (d, $J = 1.5$ Hz, 1H), 6.79 (d, $J = 7.3$ Hz, 2H), 6.97 (dd, $J = 7.3, 7.6$ Hz, 1H), 7.11 (dd, $J = 7.3, 7.3$ Hz, 2H), 7.21–7.26 (m, 3H), 7.32–7.36 (m, 3H), 7.56 (d, $J = 7.8$ Hz, 1H), 7.70 (d, $J = 8.3$ Hz, 2H), 7.78 (d, $J = 7.8$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 60.4, 110.0, 113.5, 119.9, 121.4, 124.1, 124.3, 126.8, 127.4, 127.69, 127.72, 127.8, 129.9, 135.3, 135.4, 136.1, 138.7, 140.8, 144.8, 149.6, 153.2. HRMS (FAB): calcd for $C_{30}H_{22}NO_2S$ ($M+H^+$), 460.1371, Found 460.1382.

Spiro[fluorene-9,4'(1'*H*)-indeno[1,2-*b*]pyrrole (sp-FIP)

To a solution of **3a** (7.52 g, 16.4 mmol) in THF (300 mL) and MeOH (100 mL) was added 10% aqueous solution of NaOH (66 mL), and the solution was stirred at 65 °C for 3 h. After cooling to ambient temperature, MeOH was removed under reduced pressure and the residue was extracted with $CHCl_3$ (3 \times 20 mL). The organic layers were combined, washed with water (2 \times 50 mL) and brine (50 mL), and dried over $MgSO_4$. The solvents were removed under reduced pressure to give brown solid. The crude product was purified by washing with $CHCl_3$ –hexane (1:1) and the filtrate was purified with column chromatography on SiO_2 (EtOAc–hexane, 1:15) to give **sp-FIP** (4.96 g, 99%) as a pale blue solid; mp 183.5–184.5 °C. IR (KBr) 748, 1444, 1606, 3060, 3414 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 5.79 (dd, $J = 1.7, 2.7$ Hz, 1H), 6.54 (d, $J = 7.7$ Hz, 1H), 6.80–6.86 (m, 4H), 7.11 (dd, $J = 7.3, 7.3$ Hz, 2H), 7.19 (dd, $J = 7.3, 7.5$ Hz, 1H), 7.31–7.36 (m, 3H), 7.80 (d, $J = 7.3$ Hz, 2H), 8.41 (br s, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 60.7, 103.9, 115.8, 119.8, 121.9, 123.6, 123.8, 124.3, 127.0, 127.4, 127.5, 133.7, 135.4, 137.8, 141.7, 148.5, 153.0. HRMS (FAB): calcd for $C_{23}H_{16}N$ ($M+H^+$), 306.1283, Found 306.1288.

A typical procedure for synthesis of 4a–e.

To a solution of **sp-FIP** (611 mg, 2.00 mmol) and aldehyde (1.00 mmol) in dry CH_2Cl_2 (20 mL)

was added two drops of TFA, and the solution was stirred at room temperature for 2–6 h under nitrogen atmosphere. The reaction mixture was quenched with 5% aqueous solution of NaHCO₃ (25 mL) and extracted with CHCl₃ (3 × 10 mL). The organic layers were combined, washed with brine (2 × 15 mL), and dried over MgSO₄. The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO₂ (EtOAc–hexane, 1:15) to afford **4**.

4a: A purple solid (86% yield); mp >300 °C. IR (KBr) 729, 747, 1280, 1338, 1444, 1474, 1520, 1604, 3059, 3436 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 2.90 (s, 6H), 5.38 (s, 1H), 5.52 (s, 2H), 6.49 (d, *J* = 7.7 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 6.75–6.85 (m, 6H), 7.07–7.19 (m, 10H), 7.32 (dd, *J* = 7.3, 7.3 Hz, 4H), 7.77 (d, *J* = 7.7 Hz, 4H), 8.15 (br s, 2H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 40.5, 44.6, 60.9, 103.1, 112.6, 115.6, 119.8, 123.6, 123.8, 123.9, 126.9, 127.3, 127.5, 129.0, 129.2, 133.6, 135.5, 137.2, 137.7, 141.6, 148.5, 149.5, 152.5. HRMS (FAB): calcd for C₅₅H₄₀N₃ (M+H⁺), 742.3222, Found 742.3237.

4b: A bluish purple solid (quantitative yield); mp >300 °C. IR (KBr) 729, 747, 1031, 1175, 1250, 1445, 1474, 1509, 1605, 3060, 3419 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 3.76 (s, 3H), 5.44 (s, 1H), 5.51 (s, 2H), 6.48 (d, *J* = 7.7 Hz, 2H), 6.77–6.86 (m, 8H), 7.08–7.21 (m, 10H), 7.32 (dd, *J* = 7.3, 7.7 Hz, 4H), 7.78 (d, *J* = 7.7 Hz, 4H), 8.17 (br s, 2H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 44.8, 55.2, 60.9, 103.3, 114.1, 115.7, 119.8, 123.67, 123.74, 124.1, 127.0, 127.4, 127.5, 129.5, 133.4, 133.7, 135.4, 137.1, 137.4, 141.7, 148.4, 152.6, 158.6. HRMS (FAB): calcd for C₅₄H₃₇N₂O (M+H⁺), 729.2906, Found 729.2916.

4c: A bluish purple solid (66% yield); mp >300 °C. IR (KBr) 728, 746, 1280, 1444, 1474, 1510, 1605, 3058, 3410 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 2.30 (s, 3H), 5.45 (s, 1H), 5.52 (s, 2H), 6.48 (d, *J* = 7.7 Hz, 2H), 6.77–6.85 (m, 6H), 7.08–7.21 (m, 12H), 7.33 (dd, *J* = 7.3, 7.5 Hz, 4H), 7.78 (d, *J* = 7.3 Hz, 4H), 8.17 (br s, 2H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 21.0, 45.2, 60.9, 103.3, 115.7, 119.8,

123.6, 123.8, 124.1, 127.0, 127.4, 127.5, 128.4, 129.4, 133.6, 135.4, 136.7, 137.0, 137.4, 138.4, 141.7, 148.4, 152.6. HRMS (FAB): calcd for $C_{54}H_{37}N_2$ ($M+H^+$), 713.2957, Found 713.2977.

4d: A bluish purple solid (54% yield); mp >300 °C. IR (KBr) 728, 746, 1280, 1444, 1486, 1606, 3059, 3411 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 5.41 (s, 1H), 5.48 (s, 2H), 6.49 (d, J = 7.3 Hz, 2H), 6.78–6.84 (m, 6H), 7.05–7.37 (m, 16H), 7.78 (d, J = 7.3 Hz, 4H), 8.18 (br s, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 45.0, 60.9, 103.6, 115.8, 119.9, 121.0, 123.6, 123.7, 124.3, 127.0, 127.46, 127.55, 130.2, 131.7, 133.8, 135.3, 136.1, 137.7, 140.4, 141.7, 148.2, 152.6. HRMS (FAB): calcd for $C_{53}H_{33}^{79}BrN_2$ (M^+), 776.1827, Found 776.1838.

4e: A pale purple solid (70% yield); mp >300 °C. IR (KBr) 747, 1104, 1281, 1444, 1608, 1720, 3056, 3415 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$) δ = 3.86 (s, 3H), 5.50 (s, 2H), 5.53 (s, 1H), 6.50 (d, J = 7.3 Hz, 2H), 6.65–6.85 (m, 6H), 7.09–7.14 (m, 6H), 7.22–7.36 (m, 8H), 7.78 (d, J = 7.3 Hz, 4H), 7.92 (d, J = 8.1 Hz, 2H), 8.27 (br s, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 45.6, 52.1, 60.9, 103.7, 115.8, 119.9, 123.6, 123.7, 124.4, 127.1, 127.5, 127.6, 128.5, 129.0, 130.0, 133.8, 135.2, 135.7, 137.8, 141.7, 146.6, 148.2, 152.6, 166.7. HRMS (FAB): calcd for $C_{55}H_{37}O_2N_2$ ($M+H^+$), 757.2855, Found 757.2858.

A typical procedure for synthesis of BODIPY dyes **5a–e**.

To a solution of **4a–e** (0.52 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise DDQ (119 mg, 0.52 mmol) in dry CH_2Cl_2 (10 mL) and the solution was stirred at room temperature for 1 h under nitrogen atmosphere. Et_3N (0.42 mL, 3.01 mmol) was then added, followed by an addition of 47% of $BF_3 \cdot OEt$ (0.83 mL, 3.05 mmol). After stirring for 3 h, the reaction mixture was quenched with water (20 mL). The organic layer was washed with brine (2×20 mL), and dried over Na_2SO_4 . The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO_2 ($CHCl_3$ –hexane, 1:3) to afford **5a–e**.

5a: A purple solid (59% yield); mp >300 °C. IR (KBr) 747, 1068, 1098, 1196, 1268, 1338, 1364, 1402, 1464, 1556, 1601 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 2.87 (s, 6H), 6.31 (s, 2H), 6.52 (d, *J* = 8.3 Hz, 2H), 6.63 (d, *J* = 7.3 Hz, 2H), 6.96 (d, *J* = 7.3 Hz, 4H), 7.14–7.19 (m, 6H), 7.27 (d, *J* = 8.8 Hz, 2H), 7.36 (dd, *J* = 7.3, 7.3 Hz, 4H), 7.49 (dd, *J* = 7.3, 7.7 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 4H), 8.49 (d, *J* = 7.3 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 40.0, 59.8, 111.3, 120.0, 120.6, 121.9, 124.08, 124.12, 124.2, 127.9 (two peaks are overlapped), 128.6, 129.9, 132.2, 132.9, 140.8, 141.3, 142.5, 143.5, 148.4, 151.6, 156.3, 160.2. HRMS (FAB): calcd for C₅₅H₃₆N₃F₂B (M⁺), 787.2980, Found 787.2959.

5b: A dark brown solid (73% yield); mp >300 °C. IR (KBr) 756, 1034, 1065, 1096, 1200, 1263, 1334, 1402, 1447, 1469, 1552, 1603 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 3.69 (s, 3H), 6.22 (s, 2H), 6.63 (d, *J* = 7.8 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 4H), 7.14–7.19 (m, 6H), 7.29 (d, *J* = 8.8 Hz, 2H), 7.36 (dd, *J* = 7.6, 7.8 Hz, 4H), 7.50 (dd, *J* = 7.6, 7.8 Hz, 2H), 7.79 (d, *J* = 7.3 Hz, 4H), 8.50 (d, *J* = 7.3 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 55.3, 59.7, 113.7, 120.0, 120.6, 124.17, 124.21, 124.3, 126.5, 127.9, 128.0, 128.7, 130.4, 131.9, 132.6, 141.1, 141.3, 142.1, 142.9, 148.2, 156.6, 161.0, 161.3. HRMS (FAB): calcd for C₅₄H₃₄ON₂F₂B (M+H⁺), 775.2741, Found 775.2733.

5c: A dark brown solid (61% yield); mp >300 °C. IR (KBr) 756, 1065, 1097, 1200, 1262, 1334, 1402, 1447, 1469, 1553, 1602 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 2.24 (s, 3H), 6.20 (s, 2H), 6.64 (d, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 4H), 7.05 (d, *J* = 7.8 Hz, 2H), 7.15–7.26 (m, 8H), 7.36 (dd, *J* = 7.3, 7.3 Hz, 4H), 7.51 (dd, *J* = 7.6, 7.8 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 4H), 8.49 (d, *J* = 7.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 21.2, 59.7, 120.0, 120.7, 124.17, 124.23, 124.3, 127.9, 128.0, 128.7, 128.8, 130.3, 130.4, 131.2, 132.5, 140.1, 141.1, 141.3, 142.4, 143.0, 148.2, 156.7, 161.5. HRMS (FAB): calcd for C₅₄H₃₃N₂F₂B (M⁺), 758.2714, Found 758.2708.

5d: A dark brown solid (59% yield); mp >300 °C. IR (KBr) 738, 761, 1065, 1096, 1196, 1262, 1333, 1401, 1447, 1469, 1552, 1601 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 6.15 (s, 2H), 6.65 (d, *J* = 7.8 Hz,

The reaction mixture was diluted with cold water (80 mL) and extracted with CH₂Cl₂ (4 × 15 mL). The organic layers were combined, washed with saturated aqueous solution of NaHCO₃ (2 × 50 mL) and brine (50 mL), and dried over MgSO₄. The solvents were removed under reduced pressure, and the residue was purified with GPC (CHCl₃) to afford **10** (666 mg, 11%) as a pale yellow oil; mp 97.8–98.7 °C. IR (KBr) 589, 681, 803, 1058, 1173, 1357, 1596, 2964 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ = 1.67 (s, 6H), 2.40 (s, 3H), 5.91 (dd, *J* = 1.8, 3.3 Hz, 1H), 6.88 (dd, *J* = 1.8, 1.8 Hz, 1H), 7.02–7.07 (m, 2H), 7.24–7.29 (m, 3H), 7.44 (dd, *J* = 1.5, 8.1 Hz, 1H), 7.50 (dd, *J* = 1.8, 8.1 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H). ¹³C NMR (75.5 MHz, CDCl₃) δ = 21.6, 29.7, 40.0, 113.6, 117.5, 120.9, 123.7, 126.7, 127.2, 128.0, 129.7, 135.5, 136.5, 138.3, 144.6, 146.0. HRMS (FAB): calcd for C₂₀H₂₁O₂N⁸¹BrS (M+H⁺), 420.0457, Found 420.0451.

4,4-Dimethyl-1-tosyl-1,4-dihydroindeno[1,2-*b*]pyrrole (**11**)

A flame dried Schlenk flask was charged with **10** (604 mg, 1.44 mmol), K₂CO₃ (399 mg, 2.88 mmol), Pd(PPh₃)₄ (50.2 mg, 0.0434 mmol), and dry DMF (15 mL) under nitrogen atmosphere. The solution was stirred at 100 °C for 13 h. The reaction mixture was cooled down to room temperature and filtered through a short silica gel pad. After an addition of CH₂Cl₂ (20 mL), the filtrate was washed with 10% aqueous solution of NaCl (5 × 40 mL), and dried over MgSO₄. The solvents were removed under reduced pressure to give a pale brown solid. The crude product was purified by GPC (CHCl₃) to give **11** (254 mg, 52%) as a colorless oil. IR (neat) 539, 768, 1051, 1363, 1597, 2359, 2964 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ = 1.36 (s, 6H), 2.34 (s, 3H), 6.31 (d, *J* = 3.3 Hz, 1H), 7.14–7.32, (m, 6H), 7.75 (d, *J* = 8.4 Hz, 2H), 8.03 (d, *J* = 7.3 Hz, 1H). ¹³C NMR (75.5 MHz, CDCl₃) δ = 21.6, 25.8, 42.0, 107.7, 119.4, 122.2, 124.8, 125.9, 126.7, 127.0, 130.0, 132.2, 134.4, 136.1, 144.8, 145.9, 157.1. HRMS (FAB): calcd for C₂₀H₁₉NO₂S (M⁺), 337.1137, Found 337.1130.

4,4-Dimethyl-1,4-dihydroindeno[1,2-*b*]pyrrole (**12**)

To a solution of **11** (253 mg, 0.750 mmol) in THF (7 mL) and MeOH (3.5 mL) was added 10%

aqueous solution of NaOH (3 mL), and the solution was stirred at 65 °C for 7 h. After cooling to ambient temperature, the reaction mixture was diluted with cold water (10 mL) and MeOH was removed under reduced pressure. The residue was extracted with EtOAc (3 × 5 mL). The organic layers were combined, washed with brine (2 × 20 mL), and dried over MgSO₄. The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO₂ (EtOAc–hexane, 1:3) to afford **12** (101 mg, 73%) as a pale blue solid; mp 130.6–131.3 °C. IR (KBr) 711, 754, 1063, 1454, 1610, 2959, 3370 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ = 1.45 (s, 6H), 6.21 (dd, *J* = 1.8, 2.8 Hz, 1H), 6.82 (dd, *J* = 2.4, 2.4 Hz, 1H), 7.06–7.11 (m, 1H), 7.17–7.25 (m, 2H), 7.33 (d, *J* = 7.3 Hz, 1H), 8.22 (br s, 1H). ¹³C NMR (75.5 MHz, CDCl₃) δ = 26.6, 42.4, 102.9, 115.9, 121.2, 122.5, 123.6, 126.4, 133.5, 134.0, 140.4, 157.5. HRMS (FAB): calcd for C₁₃H₁₄N (M+H⁺), 184.1126, Found 184.1122.

BODIPY Dye 6

To a solution of **12** (94.8 mg, 0.517 mmol) in dry CH₂Cl₂ (6 mL) was added two drops of TFA, and the solution was stirred at room temperature for 2 h under nitrogen atmosphere. The reaction mixture was quenched with saturated aqueous solution of NaHCO₃ (10 mL) and extracted with CH₂Cl₂ (3 × 5 mL). The organic layers were combined, washed with brine (2 × 20 mL), and dried over MgSO₄. The solvents were removed under reduced pressure, and the residue was partially purified with column chromatography on SiO₂ (CH₂Cl₂–hexane, 4:1) to afford a crude product (49.7 mg) as a blue solid. The crude product was then dissolved in dry CH₂Cl₂ (8 mL). After an addition of DDQ (23.8 mg, 0.105 mmol) in dry CH₂Cl₂ (6 mL), the solution was stirred at room temperature for 1 h under nitrogen atmosphere. *i*Pr₂NEt₂ (0.105 mL, 0.603 mmol) and BF₃·OEt₂ (0.165 mL, 0.606 mmol) were successively added and after 4 h, the reaction mixture was washed with 10% aqueous solution of NaCl (4 × 20 mL), and dried over Na₂SO₄. The solvents were removed under reduced pressure, and the residue was partially purified with column chromatography on SiO₂ (CH₂Cl₂–hexane, 1:3) to afford **6** (30.1 mg, 56%) as a dark brown solid; mp >300 °C. IR (KBr) 759, 1060, 1088, 1278,

1335, 1552, 1603, 2966 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ = 1.47 (s, 12H), 3.92 (s, 3H), 6.55 (s, 2H), 7.07 (d, J = 8.8 Hz, 2H), 7.38–7.45 (m, 6H), 7.56 (d, J = 8.4 Hz, 2H), 8.30 (d, J = 7.0 Hz, 2H). ^{13}C NMR (75.5 MHz, CDCl_3) δ = 27.1, 41.9, 55.5, 113.8, 119.3, 122.7, 124.2, 127.2, 127.9, 129.7, 130.8, 132.0, 140.6, 141.1, 148.6, 158.8, 160.87, 160.91. HRMS (FAB): calcd for $\text{C}_{34}\text{H}_{29}\text{ON}_2\text{F}_2\text{B}$ (M^+), 530.2347, Found 530.2351.

References

- 1) Arts, H. J.; Kranenburg, M.; Meijers, R. H. A. M.; Ijpeij, E. G.; Gruter, G. J. M.; Beijer, F. H. EP1059300 (A1) **2000**.
- 2) Sigmundová, I.; Uhlár, J.; Toma, Š. *Synth. Commun.* **2004**, *34*, 3667–3672.

Data of X-ray crystallographic analysis:

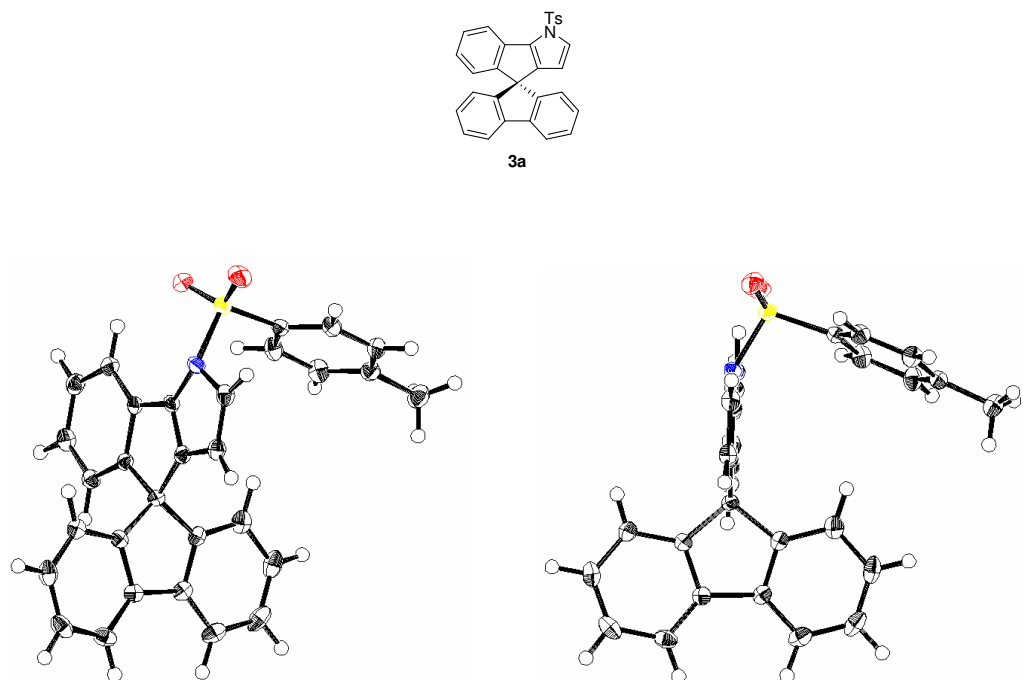


Figure S1. ORTEP drawings of **3a**.

Table S1. Crystal data and structure refinement for **3a**

Empirical Formula	C ₃₀ H ₂₁ N O ₂ S	
Formula Weight	459.56	
Temperature (°C)	−120	
Crystal Color, Habit	colorless, block	
Crystal Dimensions	0.40 × 0.40 × 0.20 mm	
Crystal System	triclinic	
Lattice Parameters	a = 10.327(4) Å	α = 75.268(15)°
	b = 10.808(5) Å	β = 65.992(11)°
	c = 11.555(4) Å	γ = 89.308(19)°
	V = 1133.3(8) Å ³	
Space Group	P-1 (#2)	
Z value	2	
D _{calc}	1.347 g/cm ³	
F(000)	480.00	
μ(MoKα)	1.719 cm ^{−1}	
Radiation	MoKα (λ = 0.71070 Å)	
	graphite monochromated	
2θ max	61.8°	
No. of Reflections Measured	Total: 10126	
	Unique: 5815 (R _{int} = 0.027)	
Structure Solution	Direct Methods (SIR92)	
Refinement	Full-matrix least-squares on F ²	
No. Observations (All reflections)	5815	
No. Variables	391	
Reflection/Parameter Ratio	14.87	
Residuals: R ₁ (I>2.00σ(I))	0.0470	
Residuals: wR ₂ (All reflections)	0.0762	
Goodness-of-fit on F ²	1.097	
Max Shift/Error in Final Cycle	0.000	
Maximum peak in Final Diff. Map	0.38 e [−] /Å ³	
Minimum peak in Final Diff. Map	−0.60 e [−] /Å ³	

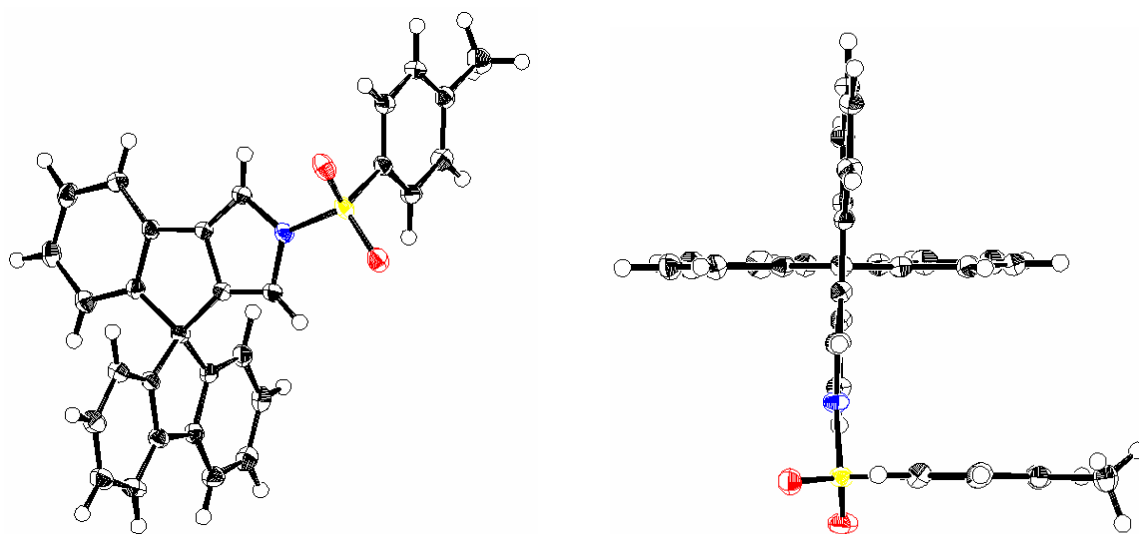
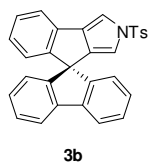
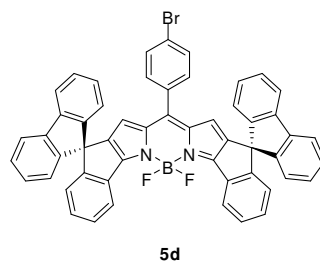


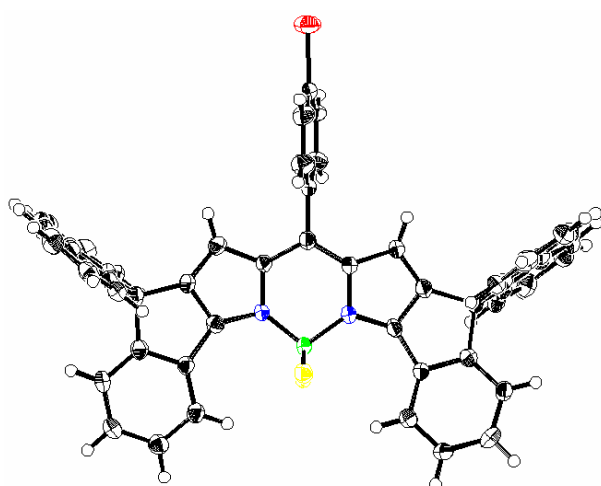
Figure S2. ORTEP drawings of **3b**.

Table S2. Crystal data and structure refinement for **3b**

Empirical Formula	C ₃₀ H ₂₁ N O ₂ S
Formula Weight	459.56
Temperature (°C)	−120
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.20 × 0.20 × 0.20 mm
Crystal System	monoclinic
Lattice Parameters	a = 12.330(4) Å b = 8.447(3) Å β = 95.906(4)° c = 21.697(7) Å V = 2247.6(13) Å ³
Space Group	<i>P</i> 2 ₁ / <i>a</i> (#14)
Z value	4
D _{calc}	1.358 g/cm ³
F(000)	960.00
μ(MoKα)	1.733 cm ^{−1}
Radiation	MoKα (λ = 0.71070 Å) graphite monochromated
2θ max	62.1°
No. of Reflections Measured	Total: 19437 Unique: 6398 (R _{int} = 0.040)
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F ²
No. Observations (All reflections)	6398
No. Variables	391
Reflection/Parameter Ratio	16.36
Residuals: R ₁ (I>2.00σ(I))	0.0475
Residuals: wR ₂ (All reflections)	0.0738
Goodness-of-fit on F ²	1.027
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.47 e [−] /Å ³
Minimum peak in Final Diff. Map	−0.45 e [−] /Å ³



a)



b)

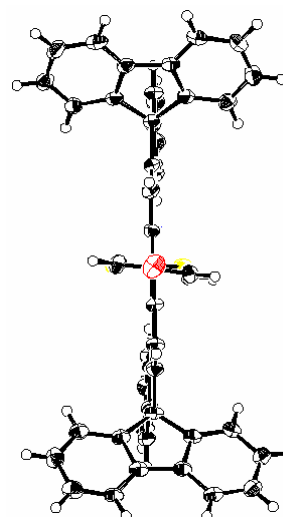


Figure S3. ORTEP drawings of **5d**. a) Front view; b) Top view. Solvent molecules have been omitted for clarity.

Table S3. Crystal data and structure refinement for **5d**

Empirical Formula	C ₅₃ H ₃₀ Br F ₂ N ₂ · C H Cl ₃
Formula Weight	942.92
Temperature (°C)	−120
Crystal Color, Habit	green, block
Crystal Dimensions	0.20 × 0.20 × 0.20 mm
Crystal System	monoclinic
Lattice Parameters	a = 12.794(3) Å b = 17.775(5) Å β = 90.835(4)° c = 18.865(5) Å V = 4289.5(20) Å ³
Space Group	<i>P</i> 2 ₁ / <i>a</i> (#14)
Z value	4
D _{calc}	1.460 g/cm ³
F(000)	1912.00
μ(MoKα)	11.982 cm ^{−1}
Radiation	MoKα (λ = 0.71070 Å) graphite monochromated
2θ max	62.1°
No. of Reflections Measured	Total: 37442 Unique: 11715 (R _{int} = 0.041)
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F ²
No. Observations (All reflections)	11715
No. Variables	590
Reflection/Parameter Ratio	19.86
Residuals: R ₁ (I > 2.00σ(I))	0.0801
Residuals: wR ₂ (All reflections)	0.1375
Goodness-of-fit on F ²	1.014
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	2.06 e [−] /Å ³
Minimum peak in Final Diff. Map	−1.65 e [−] /Å ³

Table S4. Photophysical properties of **5a** in various solvents^a

solvent	λ_{abs} [nm]	λ_{em} [nm]	ϵ_r^b	Φ_F^c
DMF	628	637	36.7	0.06
THF	627	636	7.52	0.16
CHCl ₃	631	639	4.81	0.73
benzene	631	638	2.28	0.78

^a $c = 1.00 \times 10^{-6}$ M ^b Relative dielectric constant ^c Determined by the calibrated integrating sphere system

Table S5. Cartesian atomic coordinates for the geometry optimized structure of **9** (B3LYP/6-31G(d)).

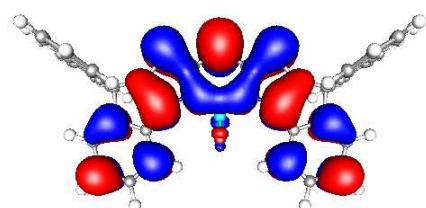
atom	x	y	z
C	0.2725108739	-1.0514936071	-1.3249863605
N	-0.6401901250	-0.0098596746	-1.0999803045
B	-0.4617015318	1.0957524529	-0.0054301105
N	0.5516944447	0.5029114922	1.0308337835
C	1.4359503516	-0.5509598336	0.7549765440
C	1.2948244978	-1.2966197104	-0.4122395345
C	-0.0884777679	-1.7437147539	-2.5207715937
F	-1.6820452530	1.3581990334	0.6140226282
C	-1.2187435989	-1.1140435675	-3.0019526871
F	0.0600345121	2.2448207299	-0.5737847811
C	0.9005493991	0.9841479904	2.2359155895
C	2.0062974717	0.2734239698	2.7637238432
C	2.3515983516	-0.6939392826	1.8414990518
C	-1.5285536060	-0.0608878059	-2.1068157682
C	-2.2158260134	-1.1555217286	-4.1439447610
C	-3.1300971042	0.0278168165	-3.7514268712
C	0.4788377045	2.0226488862	3.1529558097
C	1.3548238969	1.9572889617	4.2667245876
C	2.4044906427	0.8322111659	4.1162175282
C	-0.5569069025	2.9623618745	3.1056977806
C	-0.6956464155	3.8469990882	4.1748611698
C	0.1747211520	3.7914205371	5.2705753833
C	1.2032047629	2.8428041311	5.3242643462
C	-2.7100922406	0.6507340099	-2.5482332356
C	-4.2494573212	0.4970019009	-4.4240439994
C	-4.9509186515	1.5863185736	-3.8931249091
C	-4.5406730327	2.1928396122	-2.6993707620
C	-3.4189999008	1.7310682435	-2.0112147571
H	1.9856751600	-2.1119840887	-0.6024569736
H	0.4405400052	-2.5963675261	-2.9263556797
H	3.1375899265	-1.4360297228	1.8952952882
C	-1.5914802841	-1.0050799844	-5.5353533280
C	-2.9692324350	-2.4816459752	-4.2913546089
C	3.8498105465	1.3358777009	4.1925611009
C	2.3757596547	-0.1821680247	5.2643316773
H	-1.2352976818	2.9825398538	2.2606128711

H	-1.4916353795	4.5863094822	4.1585655001
H	0.0483587787	4.4901407627	6.0932208368
H	1.8706665552	2.8007146389	6.1806085133
H	-4.5772829882	0.0267221622	-5.3470658777
H	-5.8281715717	1.9619999243	-4.4129458430
H	-5.1051850995	3.0317432441	-2.3018652148
H	-3.1019999646	2.1794815584	-1.0767491858
C	-0.7770843236	0.0136002176	-6.0144011169
C	-1.9488093821	-2.0895570784	-6.3584762882
C	-3.7335199614	-3.154624609	-3.3461483236
C	-2.8022082410	-3.0045857985	-5.5876398718
C	1.3211526199	-0.9800773871	5.6904717862
C	3.6271432872	-0.2385850353	5.9066515560
C	4.4833241996	2.2767678574	3.3901752141
C	4.5403413411	0.7022017445	5.2427649095
C	-1.4876859483	-2.1565075546	-7.6748846811
C	-3.4056930698	-4.2127903146	-5.9425518242
H	-0.5011368349	0.8499540184	-5.3775451972
C	-0.3161100251	-0.0558612062	-7.3336839692
H	-3.8612086703	-2.7499401742	-2.3455404261
C	-4.3373411139	-4.3650771121	-3.7041415158
C	-4.1739294787	-4.8882654526	-4.9916539131
H	-3.2816276505	-4.6247395713	-6.9408689568
C	-0.6693743899	-1.1319051459	-8.1556819906
H	-1.7580611424	-2.9906582189	-8.3173494788
H	-4.9381122298	-4.9027273290	-2.9756221545
H	-4.6492157264	-5.8296235259	-5.2543700694
H	0.3218286966	0.7331497888	-7.7225187532
H	-0.3030224235	-1.1709964811	-9.1780936122
C	3.8260794283	-1.1015914422	6.9862620992
C	5.8784366737	1.0125617992	5.4942123600
H	0.3556760909	-0.9358340645	5.1932920158
C	1.5228621530	-1.8439940532	6.7725603680
C	2.7651714917	-1.9030091084	7.4138889050
H	4.7891441099	-1.1525790511	7.4878976246
H	2.9061349861	-2.5792597318	8.2528681621
H	0.7073875169	-2.4740371686	7.1172064679
C	6.5143432057	1.9587190159	4.6873546390

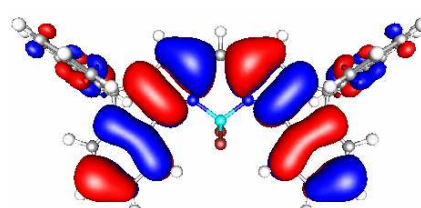
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H	3.9493056423	2.7646655120	2.5790030676
C	5.8241774144	2.5858677812	3.6439455101
H	6.3332691774	3.3194691132	3.0247917941
H	7.5555269021	2.2099694525	4.8714121012

Table S6. Results of TD-DFT calculation for **9** (TD-B3LYP/6-31G(d)//B3LYP/6-31G(d))

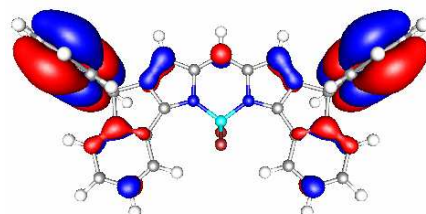
λ/nm	oscillator strength	transition	amplitude
532.00	1.0435	LUMO \leftarrow HOMO-2	-0.14168
		LUMO \leftarrow HOMO	0.58646
455.34	0.0001	LUMO \leftarrow HOMO-1	0.70195
444.47	0.1075	LUMO \leftarrow HOMO-2	0.68752



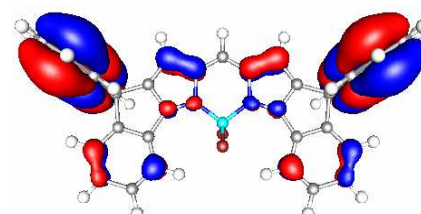
LUMO



HOMO



HOMO-1



HOMO-2

Figure S4. Molecular orbital plots for model compound **9**.

¹H and ¹³C NMR Spectra

